

Towards a quantum-chemical description of crystalline insulators: A Wannier-function-based Hartree-Fock study of Li_2O and Na_2O

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Abstract

A recently proposed approach for performing electronic-structure calculations on crystalline insulators in terms of localized orthogonal orbitals is applied to the oxides of lithium and sodium, Li_2O and Na_2O . Cohesive energies, lattice constants and bulk moduli of the aforementioned systems are determined at the Hartree-Fock level, and the corresponding values are shown to be in excellent agreement with the values obtained by a traditional Bloch-orbital-based Hartree-Fock approach. The present Wannier-function-based approach is expected to be advantageous in the treatment of electron-correlation effects in an infinite solid by conventional quantum-chemical methods.

I. INTRODUCTION

A typical quantum-chemical investigation of a system, employing a wave-function-based approach, begins with a Hartree-Fock (HF) calculation which provides an initial mean-field description of the system. Then, if the need arises, it is improved systematically — the influence of electron correlations is included by considering virtual excitations from the HF wave function. However, in such a scheme the computational effort has a rather unfavorable dependence on the size of the system and in the best-case scenario it scales roughly as N^5 , where N is the number of atoms in the system. (Only recently, attempts towards achieving linear scaling at the HF level¹, and towards exploiting the local nature of correlation effects are being made².) Because of this proliferation in the computational effort, the field of quantum chemistry is generally regarded as a science of finite systems with most of its applications limited to small or medium-sized molecules. Therefore, a naive extension of this quantum-chemical scheme to treat a system such as a three-dimensional crystalline solid is bound to run into problems. On the one hand a crystalline solid, for all practical purposes, is an infinite system. It essentially has an infinite number of electrons as well as an infinite spatial extension compared to the dimensions of a unit cell. On the other hand, the translational symmetry force its orbitals to have a delocalized itinerant character. Clearly, with such crystal orbitals, known as Bloch orbitals, it can be problematic to sum the contributions of the electron repulsion part of the Hamiltonian to convergence. In Bloch-orbital-based theories, the problems of infinite size and delocalized orbitals have been overcome at the Hartree-Fock level, nowadays, by adopting suitable procedures of integration over the Brillouin zone and lattice sums, as is done, for example, in the program CRYSTAL³. However, inclusion of electron-correlation effects by going beyond the Hartree-Fock level within a traditional quantum-chemical scheme (such as the configuration-interaction or coupled-cluster approaches) appears to be fraught with problems if one uses Bloch orbitals as a basis set. Complications will arise both due to the itinerant nature of the Bloch orbitals, as well as the infinite number of virtual states spanning the Brillouin zone that one will have to take into account, in order to compute quantities such as the correlation energy.

If one abandons the built-in translational symmetry associated with the Bloch orbitals, one can alternatively describe the electrons in a solid as being localized entities associated with the atoms or bonds constituting it. Such a localized description of electrons in a solid is much easier to understand for a chemist who is usually thinking in terms of bonds. Unlike the Bloch-orbital-based approach, a localized-orbital-oriented description of a system is not unambiguous, e.g. in the sense that one can choose either an orthogonal or a nonorthogonal set of localized orbitals. Nonorthogonal orbitals, in general, are better localized and, in principle, are also capable of describing the metallic systems where the electrons are indeed quite itinerant. Recently Bellaïche and Lévy⁴ have presented an approach, along with its application to crystalline LiH, which allows the determination of *nonorthogonal* localized Hartree-Fock orbitals of an infinite solid, from a set of finite-cluster calculations. However, with nonorthogonal orbitals a conventional quantum-chemical treatment of electron correlation such as the one based on the configuration-interaction approach is considerably more complicated. On the other hand, the orthogonal orbitals, although less localized than their nonorthogonal counterparts, offer the possibility of straightforward inclusion of correlation effects. Such an alternative approach to the description of crystalline electrons in terms

of localized orthogonal orbitals was proposed by Wannier long ago⁵, and therefore, such orbitals in the condensed-matter community have come to be known as Wannier functions. It should be intuitively obvious that it will be very difficult to describe metallic electrons in terms of Wannier functions because the orthogonality requirement will force the orbitals to extend far away from their centers, leading to their eventual delocalization⁶. However, for systems with a band gap such as semiconductors and insulators it should be possible, in principle, to satisfy both the orthogonality as well as the localization requirements as embodied in Wannier functions⁶.

Therefore, it should be clear from the preceding discussion, that if one wants to study the influence of electron correlations on an infinite solid using a traditional wave-function-based approach, it is mandatory that one first obtains a HF representation of the system in terms of Wannier functions. This goal can be achieved by first performing a HF calculation for the infinite crystal using a Bloch-orbital-based approach, and then localizing the Bloch orbitals using one of the many available localization schemes⁷ to obtain the Wannier functions⁸. However, in our previous papers^{9,10} we had presented an alternative scheme which allows a direct determination of Hartree-Fock Wannier functions of a crystalline insulator. In the first paper (henceforth to be referred to as I), we had presented an outline of the formalism and used it to compute the total energy per unit cell of crystalline LiH within an LCAO scheme. In the second paper (to be called II), we gave a rigorous derivation of the approach by minimizing the total energy of an infinite crystal, and demonstrated its theoretical equivalence to a traditional Bloch-orbital-based HF approach. Additionally in II we applied the approach to obtain the HF Wannier functions of LiF and LiCl crystals which were subsequently used to compute the X-ray structure factors and directional Compton profiles. In all the cases it was demonstrated that our results were in excellent agreement with equivalent calculations performed using the CRYSTAL program, which employs a Bloch-orbital-based HF approach. All the details pertaining to the computer implementation of our LCAO-HF program were also presented in II¹⁰. Recently, we extended this approach to study the band structure of insulating crystals and applied it to the case of NaCl¹¹. We feel, however, that it is important for us to study the efficacy of the present approach in a variety of insulating systems. With that goal in mind, in the present paper, we present the results of our Wannier-function-based HF calculations on crystalline Li₂O and Na₂O. Both these crystals are ionic in nature with the valence Wannier functions residing on O²⁻. However, O²⁻ ion is not stable in its free form and becomes stabilized in the solid state only due to the crystal field. Therefore, we believe that obtaining the valence Wannier functions of compounds involving O²⁻ is a nontrivial application of our approach. Moreover, this application involves rather diffuse basis functions requiring a significant improvement of the accuracy of lattice sums with respect to our calculations described in II.

The remainder of our paper is organized as follows. In section II, we briefly review the theoretical formalism. Then in section III we present the results of our calculations for the Li₂O and Na₂O crystals. These results include cohesive energies, lattice constants and bulk moduli of the two compounds at the Hartree-Fock level. Our results are also shown to be in excellent agreement with those obtained using the CRYSTAL program. Finally, in section IV we present our conclusions.

II. THEORY

In this section we briefly review the theory behind our approach. For more detailed derivations we refer the reader to papers I and II^{9,10}. The essential idea behind the approach is that in order to describe a perfect crystalline insulator in terms of Wannier functions, one only needs to obtain the Wannier-type orbitals localized in any one of its unit cells—the orbitals localized in the rest of the unit cells being their translated copies. This fact is a consequence of translation symmetry and can be stated mathematically as

$$|\alpha(\mathbf{R}_i)\rangle = \mathcal{T}(\mathbf{R}_i)|\alpha(\mathbf{0})\rangle, \quad (1)$$

where $|\alpha(\mathbf{0})\rangle$ represents a Wannier orbital localized in the reference unit cell assumed to be located at the origin while $|\alpha(\mathbf{R}_i)\rangle$ is the corresponding orbital of the i -th unit cell located at position \mathbf{R}_i , where \mathbf{R}_i is a lattice vector. The corresponding translation is induced by the operator $\mathcal{T}(\mathbf{R}_i)$. Clearly, in a Wannier-function-based description, the entire crystal can be described by the orbital set $\{|\alpha(\mathbf{R}_j)\rangle; \alpha = 1, n_c; j = 1, N\}$, where n_c is the number of Wannier functions associated with a unit cell and N is the total number of unit cells in the crystal whose limiting value, of course, is infinity. In the following discussion Greek labels α, β, \dots , will be reserved for labeling the (occupied) Wannier orbitals of a unit cell.

Having established the fact that one needs to specify the Wannier orbitals of only one of the unit cells, we need a dynamic prescription for obtaining them. In paper I⁹ we adopted an “embedded-cluster” picture of an infinite solid to achieve that goal. In this scheme we envision the infinite crystal as a central cluster(the reference cell) embedded in the field of its environment consisting of an infinite number of self-similar unit cells arranged according to the crystal lattice. Within this picture, it is straightforward, for a *closed-shell* system, to write down the restricted Hartree-Fock (RHF) equations for the Wannier functions of the embedded cluster, under the Born-Oppenheimer approximation:

$$(T + U + \sum_{\beta} (2J_{\beta} - K_{\beta}) + \sum_{k \in \mathcal{N}} \sum_{\gamma} \lambda_{\gamma}^k |\gamma(\mathbf{R}_k)\rangle \langle \gamma(\mathbf{R}_k)|) |\alpha\rangle = \epsilon_{\alpha} |\alpha\rangle, \quad (2)$$

where $|\alpha\rangle$ stands for $|\alpha(\mathbf{0})\rangle$, an orbital centered in the reference unit cell, T represents the kinetic-energy operator, U represents the interaction of the electrons of the reference cell with the nuclei of the whole of the solid, while J_{β} , K_{β} are the conventional Coulomb and exchange operators defined as

$$\left. \begin{aligned} J_{\beta} |\alpha\rangle &= \sum_j \langle \beta(\mathbf{R}_j) | \frac{1}{r_{12}} | \beta(\mathbf{R}_j) \rangle |\alpha\rangle \\ K_{\beta} |\alpha\rangle &= \sum_j \langle \beta(\mathbf{R}_j) | \frac{1}{r_{12}} |\alpha\rangle | \beta(\mathbf{R}_j) \rangle \end{aligned} \right\}. \quad (3)$$

Although here we have outlined an intuitive derivation of Eq.(2), it can also be obtained rigorously by minimizing the total energy of the infinite solid as shown in II¹⁰. The first three terms on the left hand side of Eq.(2) constitute the conventional canonical Hartree-Fock operator while the last term plays the role of a localization potential. It involves a sum over projection operators constructed from the orbitals of the unit cells localized in the immediate neighborhood \mathcal{N} of the central cluster. For an infinitely high value of the shift parameters, λ_{γ}^k , it has a localizing effect on the orbitals of the reference cell while simultaneously making the latter orthogonal to those located in \mathcal{N} . The choice of \mathcal{N} will clearly be dictated by the

localization characteristics of the electrons of the system under consideration. It is expected to be larger for systems with smaller band gaps. In our calculations we have typically chosen \mathcal{N} to include up to third nearest-neighbor unit cells of the reference cell. The orthogonality of the orbitals contained in unit cells beyond \mathcal{N} will also be dependent upon the band gap of the system and should be automatic once the region \mathcal{N} has been chosen to be sufficiently large. Numerical values in the range 10^3 – 10^5 atomic units for the shift parameters λ_γ^k were found to be suitable.

We have adopted a linear-combination of atomic orbital (LCAO) formalism utilizing lobe-type Gaussian basis functions¹² to solve Eq.(2). Terms U , J and K appearing in Eq.(2) involve infinite lattice sums and deserve special consideration. Evaluation of these terms along with other computational aspects are discussed in detail in paper II¹⁰. It is clear that the orthogonalization of the orbitals of the reference cell to those of the region \mathcal{N} will introduce oscillations in these orbitals which are also referred to as the orthogonalization tails. In order to describe these orthogonalization tails, one needs to express the orbitals of the reference cell as linear combination of basis functions located both in the reference cell as well as in \mathcal{N} . This increases the dimension of the Fock matrix to be diagonalized as compared to a canonical Hartree-Fock program as implemented, e.g., in CRYSTAL³. This, however, does not affect the evaluation of one- and two-electron integrals (and their number) if a careful use of translational symmetry is made as discussed in II¹⁰. After the diagonalization of the Fock matrix, one is confronted with the task of choosing the occupied orbitals from the spectrum of the eigenvalues. For the ionic systems considered here, the aufbau principle was used for this purpose; in practice, one starts with a suitable guess for the Wannier functions, and iteratively solves Eq.(2) until the energy per unit cell has converged.

III. CALCULATIONS AND RESULTS

In this section we present the results of the calculations performed on crystalline Li_2O and Na_2O . These compounds have been investigated extensively at the Hartree-Fock level in a number of papers by the Torino group using their CRYSTAL program^{13,14}. Therefore, we also intend to compare our results with the most recent results of that group¹⁴. In addition, we discuss the characteristics of the O^{2-} Wannier orbitals obtained from our calculations and compare them to atomic orbitals of free oxygen (and its singly negative ion).

A. Geometry, basis set and computational parameters

All the calculations reported below have been carried out by assuming the observed anti-fluorite structure with the space group $Fm\bar{3}m$. The reference unit cell was assumed to be the primitive cell with oxygen anion placed at the origin and the two cations at the positions $(a/4, a/4, a/4)$ and $(-a/4, -a/4, -a/4)$, where a is the lattice constant.

The Torino group studied these compounds using highly-optimized extended basis sets and for the sake of comparison, we have used the most recent basis set reported by them¹⁴. It employs a (7s1p)/[2s1p] set for lithium, a (15s7p)/[4s3p] set for sodium and a (14s6p)/[4s3p] set for oxygen¹⁴. As indicated in the previous section, we have not used real Cartesian-type

Gaussian basis functions but rather their approximate counterparts obtained by forming linear combinations of lobe-type (1s) Gaussian functions^{10,12}. For the case of Li_2O the number of (contracted) basis functions per unit cell is 23 while for the case of Na_2O it is 39. However, in order to satisfy the orthogonality requirements associated with the Wannier functions, we also have to supply the basis functions located on the neighboring cells to describe the Wannier orbitals of the central cluster. As mentioned in the previous section, this neighborhood \mathcal{N} consists of up to third-nearest neighbors of the central cluster. Since for the fcc geometry, there are 42 unit cells in \mathcal{N} so defined, one has to use the basis functions of 43 unit cells including the reference cell. Thus the number of basis functions associated with the Wannier orbitals of Li_2O and Na_2O explodes to 989 and 1677 respectively. This proliferation in the number of basis functions does not affect the integral evaluation time in any way¹⁰, compared to the CRYSTAL program³, as long as the use of point-group symmetry is the same. However, it does increase the dimension of the Fock matrix to be diagonalized to the corresponding numbers, thus increasing the time needed to perform the Hartree-Fock iterations. The latter problem is not too critical, though, since contracting basis functions in \mathcal{N} to about single-zeta quality is expected to remedy this issue without adversely affecting the accuracy of the calculation.

The CRYSTAL program uses several computational parameters which determine the accuracy of the Coulomb and the exchange series. The parameter related to the Coulomb series is called ITOL1 and those related to the exchange series are called ITOL3, ITOL4 and ITOL5³. The values of 7,7,7 and 15 for these parameters for the CRYSTAL-program based calculations are generally believed to lead to well-converged results³. These values of the parameters ensure an absolute accuracy of $\approx 1.0 \times 10^{-7}$ atomic units (a.u.) in the Fock matrix elements leading to an expected accuracy of ≈ 1 milliHartree per atom in the total energy³. Therefore, to make the comparison with CRYSTAL results transparent, in our calculations also we treated the Coulomb and the exchange series in an entirely equivalent way.

B. Lattice Constant, Bulk Modulus and the Cohesive Energy

In order to optimize the lattice constant and to obtain the bulk modulus we first computed total energies per unit cell of both the compounds for different values of lattice constants which are closely spaced around the equilibrium value. As also reported in papers I and II^{9,10}, the total energies (per unit cell) obtained by us at different lattice constants agreed with the corresponding values obtained by the CRYSTAL program to within fractions of a milliHartree. We then fitted these data points to polynomials. The resulting bulk properties were found to be stable to within a fraction of a percent with respect to an increase in the degree of the polynomial considered, and are listed in table I. In the same table, lattice constants, bulk moduli, and cohesive energies for the two compounds obtained from our calculations are compared with the results of the Torino group¹⁴ and also with experiments whenever possible. Cohesive energies were obtained by subtracting the corresponding atomic Hartree-Fock energies from the equilibrium total energy per unit cell. To make the comparison with the results of the Torino group meaningful, we used the same atomic HF energies of -7.4313 a.u. (Li atom), -161.8513 a.u. (Na atom) and -74.8012 a.u. (O atom) as used in their calculations¹⁴.

With the same basis sets, our approach and that of the Torino group¹⁴ should yield identical results. A quick glance at table I reveals that the agreement for lattice constants and cohesive energies is excellent. The maximum disagreement of 1 milliHartree in the cohesive energies is well within the expected numerical accuracies of CRYSTAL³ and our program. The maximum deviation in the bulk moduli is less than 3 GPa and are to be expected for the present disagreements in total energies, since second derivatives are much more sensitive to numerical inaccuracies. We suspect that part of the reason behind these small differences in the results of the two programs could also be due to our use of lobe functions to approximate the Cartesian-type Gaussian basis functions used in the CRYSTAL program³.

The experimental value of the lattice constant of Li_2O is based on inelastic neutron scattering experiments¹⁵ performed in a temperature range 293-1603 K. The value of 4.573 Å is the zero-temperature value obtained by extrapolating the a versus T curve¹⁵. The result of the Torino group¹⁴ is in essentially exact agreement with this value while our value is 0.003 Å shorter. For Na_2O the experimental value of the lattice constant was determined to be 5.55 Å at room temperature by Zintl et al.¹⁶ in an old experiment based upon powder diffraction pattern data. Because of the lack of availability of any other measurements, Dovesi et al.¹⁴ extrapolated this to a zero-temperature value of 5.49 Å using arguments based upon trends observed in the temperature dependence of the lattice constant of NaF. Our calculated value of 5.481 Å as well as the value of 5.484 Å of the Torino group¹⁴ are both in good agreement with the above-mentioned zero-temperature value.

The extrapolated zero-temperature value of the bulk modulus of Li_2O obtained from the finite temperature data of Hull et al.¹⁵ is 89 GPa. Our value of 94.6 GPa is approximately 6% larger than this experimental value. We believe that most of this disagreement is due to missing correlation effects. In the case of Na_2O , no experimental value is available for the bulk modulus, to the best of our knowledge. However, reasonably close agreement with the results of the Torino group¹⁴, gives us confidence as to the correctness of our result.

When we compare the Hartree-Fock cohesive energies reported here to the experimental values¹⁷, we note that for Li_2O we recover $\approx 67\%$ of the total contribution while for Na_2O this fraction is about 57%. As also argued by Dovesi et al.¹⁴, most of the missing cohesive energy at the Hartree-Fock level is due to the absence of correlation effects. This belief is also substantiated by various finite-cluster-based calculations performed in our group where, by including correlation effects, typically about 95% of the experimental cohesive energy was recovered¹⁸. Therefore, the extension of the scheme of local correlation-energy increments as described in refs.¹⁸, to the case of infinite crystals, appears to be worthwhile. This task, however, is nontrivial and presently we are in the process of implementing it.

C. Wannier Functions

Now we turn to the discussion of the Hartree-Fock Wannier functions that we obtain on solving Eq.(2). Since the qualitative behavior of the Wannier functions of both compounds is expected to be the same, we will discuss only the orbitals of Li_2O . The central cluster chosen in this work consists of one primitive cell of the lattice. Therefore, for Li_2O our Hartree-Fock equations involve fourteen electrons leading to seven Wannier functions. Out of these seven functions, three correspond to low-lying 1s-type core orbitals of the three atoms in

the unit cell, while the remaining four correspond to the 2s- and 2p-type functions centered on oxygen. Since these four high-lying valence Wannier functions are responsible for most of the chemical properties of the compounds considered, we will restrict our discussion to them.

The nearest-neighbor environment of the O^{--} ion in the crystal consists of Li^+ ions located at the eight corners of a cube with coordinates $(\pm a/4, \pm a/4, \pm a/4)$, while the center of the cube at position (0,0,0) is occupied by O^{--} ion itself. This type of environment results in three 2p-type Wannier functions of the crystal, each one of which is a mixture of the $2p_x$, $2p_y$ and $2p_z$ type basis functions localized on oxygen. In Figs. 1 and 2, respectively, we present the 2s-type and one of the 2p-type Wannier functions of Li_2O crystal, localized on the O^{--} ion. The 2p-type Wannier function presented here is isotropically oriented along the body diagonals. Both the orbitals are plotted along the crystal [111] direction. Since the crystal structure of Li_2O is invariant under the parity operation, we expect the corresponding 2s- and 2p-type Wannier functions to be, respectively, symmetric and antisymmetric, under the operation of parity. This is precisely what we find when we examine those figures. In addition, we also note that both the orbitals have nodes near the positions $(\pm a/4, \pm a/4, \pm a/4)$, which correspond to the locations of the two Li atoms of the unit cell. These nodes are a consequence of the orthogonalization of the Wannier functions to the Li 1s-type core Wannier functions. The localized nature of both the Wannier functions is evident by their rapid decay as one moves away from the oxygen site. This is a rather pictorial confirmation also of the ionic character of the crystal. The noteworthy point is that apart from the presence of the orthogonality nodes which are indicative of the presence of the environment, the qualitative nature of Wannier functions is very similar to those of any molecular orbitals, thus bringing them close to the intuition of a chemist.

The simplest qualitative picture of cohesion in an ionic solid is that it is accompanied by charge transfer from one set of atoms to another, leading to cations and anions at different sites. These oppositely charged ions, in turn, are held together by the electrostatic attraction between them. For the present case of Li_2O , this would imply that the crystal consists of Li^+ and O^{--} ions in closed-shell configurations. Such a picture can be verified, e.g. by performing a Mulliken population analysis, also in a Bloch-orbital-based approach¹⁴. However, a Wannier-function-based approach provides a more direct and unambiguous view of the cohesive process. To this end we first compare the 2s orbital of the free oxygen atom (which is also plotted in Fig. 1) with the 2s-type Wannier function of Li_2O . For free oxygen atom a basis set also reported by the Torino group¹⁴ was used, which they obtained by reoptimizing the outermost exponents of the crystal basis set and by adding one more sp-type diffuse exponent (0.0867) to it. As is clear from the figure, the spatial behavior of the 2s orbital changes only in a rather subtle manner in that the corresponding Wannier function develop nodes near the positions $(\pm a/4, \pm a/4, \pm a/4)$ due to their orthogonalization to the 1s-type Wannier functions of the Li^+ ions of the unit cell located there. Apart from these orthogonality nodes, the two orbitals are remarkably similar. This is consistent with our intuitive picture in that being a lower valence orbital, one should not expect the 2s orbital to be affected appreciably by the crystal field. Therefore, we expect the effects of cohesion to be most evident in the case of the 2p-type Wannier functions. In the simple ionic picture, the O^{--} ion of the solid has a filled 2p shell. The presence of two extra electrons on oxygen will result in the 2p electrons experiencing larger on-site repulsion leading to the charge density

associated with 2p-type Wannier functions becoming more diffuse compared to the isolated atom. Using the same intuitive reasoning we expect the 2p charge density in the solid to be more diffuse even compared to the free O^- . These points are illustrated in Fig. 3 where we plot the total 2p charge density associated with the 2p-type Wannier functions of the Li_2O lattice along the $[111]$ crystal direction, and compare it with the corresponding charge densities of free O atom and free O^- ion. The orbitals of free O^- ion were obtained from a basis set which was obtained by augmenting the free atom basis set discussed earlier by one more diffuse sp-type exponent of 0.0345. The total normalized charge densities were obtained by proportionately adding the contributions of the individual charge densities of the three 2p-type orbitals of the systems under consideration. A delocalization trend is certainly obvious in the region close to the nuclei from the decreasing heights of the peaks as one compares the 2p-charge densities in the order of free O atom, free O^- ion and embedded O^{--} ion. To quantify the degree of localization of various orbitals we computed the directionally averaged expectation values of $r^2 = x^2 + y^2 + z^2$ operator for the 2p-type orbitals of free O, O^- and the corresponding Wannier functions of the Li_2O crystal. The directionally averaged values of a given system were obtained by averaging over the expectation values of the three 2p-type orbitals according to $\overline{\langle r^2 \rangle}_{2p} = (\sum_{i=1}^3 \langle r^2 \rangle_{2p_i})/3$. The obtained values for $\overline{\langle r^2 \rangle}_{2p}$ (in Bohr²) were 1.974 (free O atom), 3.038 (free O^- ion) and, 3.008 (Li_2O crystal). As expected, we find that the value of $\overline{\langle r^2 \rangle}_{2p}$ is smallest for the case of free O atom. However, when we compare the corresponding values of free O^- with those of the embedded O^{--} of the Li_2O crystal, we arrive at somewhat counter-intuitive result that the size of the 2p-type orbital of the embedded O^{--} is a little smaller than the corresponding orbital of free O^- . To account for finite-basis-set effects as well as the nonuniqueness of Wannier functions, we can perhaps say that the 2p-type orbitals of free O^- and embedded O^{--} are approximately equal. One possible objection against this finding is that our basis set for the solid-state calculations, with the most diffuse sp-type exponent of only 0.15¹⁴, is not diffuse enough to describe a doubly charged anion like O^{--} . However, we do not suspect this to be the reason behind our finding because, as discussed earlier, our Wannier functions contain basis functions not only of the atom that they are centered upon, but also the basis functions of atoms contained in up to third-nearest neighbour unit cells of the reference cell. Thus these moderately diffuse exponents located on the neighboring atoms should be able to describe the long-range behavior of the Wannier functions of the reference atoms. Moreover, since the solid state basis set has correctly predicted the lattice constant of Li_2O , we expect it to be a reasonably complete set. Our explanation of the finding, that the size of embedded O^{--} ion of the Li_2O crystal is essentially the same as that of the singly charged free O^- , is based upon a competition between the on-site repulsion and the crystal-field effects (Pauli repulsion of surrounding atoms). In our opinion, in the crystalline phase, the on-site repulsion which certainly has a delocalizing influence, is overpowered by the crystal field leading to a stable O^{--} ion whose size is comparable to that of the free O^- ion.

IV. CONCLUSIONS

In this paper we extended the application of a Wannier-function-based Hartree-Fock approach developed earlier^{9,10} to alkali oxides, Na_2O and Li_2O . State-of-the-art basis sets containing rather diffuse s- and p-type functions were used and quantities such as the equi-

librium lattice constant, bulk modulus and cohesive energy per unit cell were computed. We obtained excellent agreement with the results of a previous Hartree-Fock study carried out by the Torino group¹⁴ using their Bloch-orbital-based CRYSTAL program³. In addition, a detailed pictorial view of the cohesive process is provided by the Wannier functions of our work which comes close to the intuitive understanding of a chemist.

As far as the agreement with experimental data is concerned, it is excellent for the lattice constant. For the bulk modulus agreement is acceptable. As expected, the most severe deviation is evident in case of the cohesive energies of the two compounds where disagreement between Hartree-Fock theory and experiment is in the range of 30%—40%. This points to the importance of correlation effects, and we consider it as an advantage of our Wannier-function-based Hartree-Fock approach that it provides a natural starting-point for improvement by means of local correlation methods¹⁸. Efforts along this direction are presently underway in our group, and the results will be presented in a future publication.

REFERENCES

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- ¹ See, e.g, M. Challacombe, E. Schwegler, and J. Almlöf, J. Chem. Phys. **104**, 4685 (1996); J.C. Bruant, G.E. Scuseria, and M.J. Frisch, J. Chem. Phys. **105**, 8969 (1996).
 - ² See, e.g, C. Hampel, and H.-J. Werner, J. Chem. Phys. **104**, 6286 (1996) and references therein.
 - ³ R. Dovesi, C. Pisani, C. Roetti, M. Causa and V.R. Saunders, CRYSTAL88, Quantum Chemistry Program Exchange, Program No. 577 (Indiana University, Bloomington, IN 1989); R. Dovesi, V.R. Saunders and C. Roetti, CRYSTAL92 User Document, University of Torino, Torino, and SERC Daresbury Laboratory, Daresbury, UK, (1992).
 - ⁴ L. Bellaïche and B. Lévy, Phys. Rev. B **54**, 1575 (1996).
 - ⁵ G. Wannier, Phys. Rev. **52**, 191 (1937).
 - ⁶ W. Kohn, Phys. Rev. B **7**, 4388 (1973).
 - ⁷ J.M. Foster and S.F. Boys, Rev. Mod. Phys. **32**, 300 (1960); C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35** 457 (1963); T. L. Gilbert, in: *Molecular Orbitals in Chemistry, Physics and Biology*, ed. P.O. Löwdin and B. Pullman (Academic, New York, 1964), pp. 405-420; W.H. Adams, J. Chem. Phys. **34**, 89 (1961); *ibid.* **37**, 2009 (1962); *ibid.* **42**, 4030 (1965); J. Pipek and P.G. Mezey, *ibid.* **90**, 4916 (1989).
 - ⁸ See N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997), for a scheme aimed at obtaining maximally localized Wannier functions from Bloch orbitals using an approach similar to the Foster-Boys scheme⁷ cited above.
 - ⁹ A. Shukla, M. Dolg, H.Stoll and P. Fulde, Chem. Phys. Lett. **262**, 213 (1996).
 - ¹⁰ A. Shukla, M. Dolg, P. Fulde and H.Stoll, Phys. Rev. B **57**, 1471 (1998).
 - ¹¹ M. Albrecht, A. Shukla, M. Dolg, H. Stoll, and P. Fulde, Chem. Phys. Lett. (in press).
 - ¹² In molecular calculations lobe-type functions were suggested independently by H. Preuss, Z. Naturf. A **11**, 823 (1956) and J.L. Whitten, J. Chem. Phys. **39**, 349 (1963). They were used for the first time in solid-state calculations within the context of Bloch-orbital-based Hartree-Fock calculations by Euwema and coworkers. See, for example, R.N. Euwema, D.L. Wilhite and G.T. Surrat, Phys. Rev. B **7**, 818 (1973).
 - ¹³ R. Dovesi, Solid State Commun. **54**, 183 (1985).
 - ¹⁴ R. Dovesi, C. Roetti, C. Freyria-Fava and M. Prencipe, Chem. Phys. **156**, 11 (1991); R. Dovesi, C. Roetti, C. Freyria-Fava, E. Aprà , V.R. Saunders and N.M. Harrison, Phil. Trans. R. Soc. Lond. A **341**, 203 (1992).
 - ¹⁵ S.Hull, T.W.D. Farley, W. Hayes and M.T. Hutchings, J. Nucl. Mater. **160**, 125 (1988).
 - ¹⁶ E. Zintl, A. Harder and B. Dauth, Z. Elektrochemie **40**, 588 (1934).
 - ¹⁷ R.C. Weast, ed., The Handbook of Chemistry and Physics, 67th edn. (CRC Press, Cleveland, OH, 1986-1987).
 - ¹⁸ B. Paulus, P. Fulde and H. Stoll, Phys. Rev. B **51**, 10572 (1995); K. Doll, M. Dolg, P. Fulde and H. Stoll, Phys. Rev. B **52**, 4842 (1995); B. Paulus, P. Fulde and H. Stoll, Phys. Rev. B **54**, 2556 (1996); K. Doll, M. Dolg and H. Stoll Phys. Rev. B **54**, 13529 (1996); S. Kalvoda, B. Paulus, P. Fulde and H. Stoll, Phys. Rev. B **55**, 4027 (1997); B. Paulus, F.-J. Shi and H. Stoll, J. Phys. Cond. Matter **9**, 2745 (1997); K. Doll, M. Dolg, P. Fulde and H. Stoll, Phys. Rev. B **55**, 10282 (1997); M. Albrecht, B. Paulus and H. Stoll, Phys. Rev. B **56**, 7339 (1997); K. Doll, H. Stoll, Phys. Rev. B **56**, 10121 (1997).

FIGURES

FIG. 1. Free atom 2s orbital of oxygen and 2s-type crystal Wannier function of Li_2O localized on O^{--} plotted along the $[111]$ direction.

FIG. 2. 2p-type crystal Wannier function of Li_2O localized on O^{--} plotted along the $[111]$ direction.

FIG. 3. Charge density associated with the 2p-type Wannier functions of Li_2O localized on O^{--} , compared to the 2p charge densities of the free oxygen atom and free O^- . All the charge densities are plotted along the $[111]$ direction and are normalized to unity.

TABLES

TABLE I. Equilibrium lattice constants (in Å), bulk moduli (in GPa), and cohesive energies (in atomic units) for Na₂O and Li₂O, obtained using our approach and reported by the Torino group¹⁴. Relevant experimental data are also given for comparison.

Quantity	Method	System	
		Li ₂ O	Na ₂ O
Lattice Constant	This Work	4.570	5.481
	Torino	4.573	5.484
	Exp	4.573 ^a	5.55 ^b
			(5.49)
Bulk Modulus	This Work	94.6	61.1
	Torino	92.6	58.4
	Exp	89 ^a	—
Cohesive Energy	This Work	-0.3008	-0.1883
	Torino	-0.3005	-0.1893
	Exp	-0.4491 ^c	-0.3321 ^c

^a Ref.¹⁵.

^b Room temperature value from ref.¹⁶. The number in parentheses is the extrapolated zero-temperature value suggested by the Torino group¹⁴. For a discussion see text.

^c Ref.¹⁷.



